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(54) Title: BALLISTIC STRUCTURE

(57) Abstract

A ballistic structure is provided exhibiting increased ballistic performance by virtue of the use of high tenacity para-aramid yarn having a particular linear density of 300 to 750 denier, and a tenacity of at least 28 grams per denier.

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TITLE

Ballistic Structure

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a ballistic structure which provides improved ballistic protection due to use of a particularly specified para-aramid yarn having a combination of high tenacity and moderate linear density.

Description of the Prior Art

United States Patent No. 4,965,033, issued October 23, 1990 on the application of Chiou, discloses a process for spinning aromatic polyamide fibers utilizing a high mass, jetted, flow of coagulating liquid.

United States Patent No. 3,767,756, issued October 23, 1973 on the application of Blades, and No. 5,173,236, issued December 22, 1992 on the application of Yang, disclose spinning aromatic polyamide fibers utilizing spinnerets having capillaries from 0.025 to 0.25 millimeters (1 to 10 mils) and less than 0.064 (2.5 mils), respectively, and drying such fibers at tensions on the order of 0.3 grams per denier.

United States Patent No. 4,726,922, issued February 23, 1988 on the application of Cochran and Yang, discloses spinning aromatic polyamide fibers and drying them under tension of 3 to 7 grams per denier to increase strength of the fibers.

Melliand Textilberichte, Structure and Action of Bullet-Resistant Protective Vests, Vol. 463-8 (1981) discloses that fabrics of fine aramid yarns, for example, 220 or 440 dtex, provide better ballistic protection than fabrics made from coarser yarns.

SUMMARY OF THE INVENTION

There is provided a ballistic protective fabric comprising yarn of at least 28 grams per denier (gpd) tenacity with a linear density of from 300 to 750 denier, which, when tested for V_{50} in accordance with MIL-STD-662e using 9mm full metal jacket hand-gun bullets weighing 124 grains, in layers to yield an areal density of 3.4 kilograms per square meter (0.7 pounds per square foot), exhibits a V_{50} of greater than 442 meters per second (1450 feet per second).

The fabric is made using yarn of poly(p-phenylene terephthalate) having a tenacity of at least 28 gpd (25 cN/dtex) which can be made by a process comprising the steps of: (a) extruding filaments of an acid solution containing at least 30 grams per 100 milliliters of acid of poly(p-phenylene terephthalamide) having an inherent viscosity of at least 4, out of a spinneret and through a layer of inert noncoagulating fluid into a coagulating bath and then through a spin tube along with overflowing coagulating liquid; (b) jetting additional coagulating liquid symmetrically about the filaments in a downward direction forming an angle of 0° to 85° with respect to the filaments within about 2.0 milliseconds from the time the filaments enter the spin tube, (i) maintaining a ratio of the mass flow rate of combined overflowing and jetted coagulating liquid to mass flow rate of the filaments of greater than about 250, (ii) maintaining a momentum ratio of jetted to overflowing coagulating liquids of greater than about 6.0, (iii) maintaining an average linear velocity of combined overflowing and jetted coagulating liquid in the spin tube which is less than the velocity of the filaments exiting from the spin tube, and (iv) maintaining constant the flow rates of both the jetted and the overflowing coagulating liquids; and (c) drying the filaments,

wherein the spinneret has capillaries with diameters of no more than 0.051 millimeter (2 mils) and

the filaments are dried under a tension of at least 3.0 gpd.

BRIEF DESCRIPTION OF THE DRAWING

The Figure is a three dimensional graphic representation of ballistic performance data from the Examples herein.

DETAILED DESCRIPTION OF THE INVENTION

Protective garments and other ballistic materials have long been made using p-aramid fibers. P-aramid fibers are extremely strong on a weight basis and provide good ballistic protection with a relatively high degree of comfort.

There has been great effort expended in developing yarns and fabrics with improved ballistic performance because even small improvements save the lives of users of ballistic garments. Each improvement is hard-won and highly significant. The present invention represents an improvement in ballistic performance, measured by V_{50}.

It has been discovered that improved ballistic performance can be obtained by using aramid yarns having a combination of especially high tenacity and a linear density within a particular range.

The physical parameters which have been believed to be important for ballistic performance in aramid yarns are tenacity, modulus, and elongation to break. While those parameters are still held to be important, this inventor has discovered that yarns of especially high tenacity -- greater than 28 grams per denier -- used in a linear density range of about 300 to 750, preferably 400 to 600 denier, will provide surprising improvement in ballistic performance.

It has been discovered that the performance of ballistic fabrics is at an optimum in the yarn denier range of about 300 to 750 and is highest in the denier range of 400 to 600. It is believed, for reasons that

are not fully understood, that ballistic fabrics having yarns of less than 300 denier and more than 750 denier exhibit ballistic performance lower than the performance of fabrics made from yarns inside that range.

As a general rule, ballistic performance is believed to be improved by using yarns exhibiting increased tenacity; and the inventor has discovered that ballistic fabrics made from yarns with tenacity of 28 to 32 or as much as 33 grams per denier yield the high ballistic performance of this invention.

The yarns of this invention can be made from individual filaments which have a relatively wide range of denier per filament of less than one to more than two. Yarns with filaments having a denier of 1.5 or less have been found to be softer and more comfortable when used in protective garments.

Ballistic fabrics of this invention are made with yarns which are woven or laid into fabrics; and the fabrics are formed into garments or other structures for ballistics protection. The kind of fabric, whether woven or not, and, if woven, of whatever weave customarily used in ballistics applications, to which the yarn is applied is not important to realize the benefit of the invention. That is, for any fabric, ballistic performance obtained using the yarn of this invention will be improved over that obtained using a similar yarn having a lower tenacity or a linear density outside the specified range.

Body armor using ballistic protective fabrics is usually made with several layers laid or sewn together to yield a laminated structure. The laminated structure can include additional layers of other materials, such as decorative or moisture resistant covering fabrics or other shock absorbing materials. The form of the laminated structure and whether or not it includes additional layers of other materials is not important to realization of the improved ballistic performance of this invention.

Yarns of the present invention have a tenacity of at least 28 gpd. These yarns can be made, generally, in accordance with a process as disclosed in United States Patents No. 3,767,756 and 4,965,033 utilizing poly(p-phenylene terephthalamide) (PPD-T) having an inherent viscosity of at least 4.0 dissolved in sulfuric acid having a concentration of at least 98%. A PPD-T solution is extruded from a spinneret, through an air gap and into a coagulating bath. The spinneret has capillaries with a diameter of 0.051 millimeter (2.0 mils) or less. It has been found that capillaries of more than 0.051 millimeter (2 mils) yield fiber filaments which are believed to have less molecular orientation resulting in decreased strength and, therefore, not as strong as filaments which are made using capillaries of smaller diameter. As a practical matter, capillaries of less than about 0.025 millimeter (1 mil) are difficult to use and may not yield fibers of acceptable quality.

The fibers, once spun and passed through the coagulating bath, are washed and dried to complete the manufacture. Fibers must be thoroughly washed to remove all traces of acid and eliminate acid-related fiber degradation. Water alone or combinations of water and alkaline solutions can be used for fiber washing. A convenient method for washing is to spray the threadline, as it leaves the coagulating bath on rolls with aqueous alkaline solutions (e.g. saturated $NaHCO_3$ or 0.05 N NaOH), to reduce the acid content to about 0.01% (on a dry fiber basis).

The fibers can conveniently be dried on heated rolls (e.g. 160°C). The preferred washing method is to wash the fibers with a spray and pass them continuously to dryer rolls maintained at about 150°C. It is preferred that the fibers be conducted directly from the washing to the drying without subjecting the fibers to any dewatering processes.

One important element of this process involves drying the fibers under high tension of from about 3.0 to

7.0 gpd. Drying tensions of less than 3.0 gpd result in fibers which have reduced molecular orientation resulting in reduced strength and drying tensions of greater than 7.0 gpd cause excessive threadline breakage and related operational difficulties. Drying tensions of about 3.5 to 6.0 gpd are particularly preferred.

Test Methods

Ballistic Limit

Ballistic tests of the composite samples are conducted to determine the ballistic limit (V_{50}) in accordance with MIL-STD-662e, except in the selection of projectiles, as follows: A lay-up to be tested is placed in a sample mount to hold the lay-up taut and perpendicular to the path of test projectiles. The projectiles are 9mm full metal jacket hand-gun bullets weighing 124 grains, and are propelled from a test barrel capable of firing the projectiles at different velocities. The first firing for each lay-up is for a projectile velocity estimated to be the likely ballistic limit (V_{50}). When the first firing yields a complete lay-up penetration, the next firing is for a projectile velocity of about 50 feet per second less in order to obtain a partial penetration of the lay-up. On the other hand, when the first firing yields no penetration or partial penetration, the next firing is for a velocity of about 50 feet per second more in order to obtain a complete penetration. After obtaining one partial and one complete projectile penetration, subsequent velocity increases or decreases of about 50 feet per second are used until enough firings are made to determine the ballistic limit (V_{50}) for that lay-up.

The ballistic limit (V_{50}) is calculated by finding the arithmetic mean of an equal number of five of the highest partial penetration impact velocities and five of the lowest complete penetration impact velocities, provided that there is not more than 125 feet

per second between the highest and lowest individual impact velocities.

Tensile Properties

Tenacity is reported as breaking stress divided by linear density. Modulus is reported as the slope of the initial stress/strain curve converted to the same units as tenacity. Elongation is the percent increase in length at break. Both tenacity and modulus are first computed in g/denier units which, when multiplied by 0.8826, yield dN/tex units. Each reported measurement is the average of 10 breaks.

Denier is the weight, in grams, of 9000 meters and dtex is the weight, in grams, of 10,000 meters of yarn or filament.

Tensile properties for yarns are measured at 24°C and 55% relative humidity after conditioning under the test conditions for a minimum of 14 hours. Before testing, each yarn is twisted to a 1.1 twist multiplier (for example, nominal 1500 denier yarn is twisted about 0.8 turn/centimeter). Each twisted specimen has a test length of 25.4 cm and is elongated 50% per minute (based on the original unstretched length) using a typical recording stress/strain device.

The twist multiplier (TM) of a yarn is defined as:

$$TM = \frac{(tpi)\ (Denier)^{1/2}}{73} = \frac{(tpc)\ (dtex)^{1/2}}{30.3}$$

Wherein tpi = turns per inch; and
tpc = turns per centimeter.

Tensile properties for yarns are different from and lower than tensile properties for individual filaments and such values for yarns cannot successfully and accurately be estimated from filament values.

EXAMPLES

In the following examples, poly(para-phyenylene terephthalamide) (PPD-T) having an inherent viscosity of about 6.3 dL/g before solutioning and about 5.5 dL/g in fiber form was spun into apparatus as illustrated in U.S. Patent No. 4,340,559 using tray G. The diameter of the spin tube was 0.76 cm (0.3 inch) and jets of 0.21 and 0.42 millimeters (8 and 16 mils) were employed with an angle of 30 degrees between the jetted stream and the threadline. The solvent employed in making spin dope was about 100.1% sulfuric acid and the concentration of polymer in the spin dope of about 19.4 wt.%.

As indicated in TABLE I, the spinnerets of 0.051 and 0.064 millimeters (2.0 and 2.5 mils) were employed. The number of capillaries of spinnerets employed included 133, 266, 400, 500, 560 and 666 capillaries. The air-gap, i.e., the distance of filament travel from the exit face of the spinneret to the first contact with coagulating liquid, was about 0.635 cm (0.25 inch). The coagulating liquid was maintained at about 3°C. Yarn tensions of about 1.0 gpd during washing and neutralization were employed for all of the examples described below.

Examples of the invention utilized spinnerets with capillaries of 0.051 millimeter. The yarns were dried under tension of greater than 3 grams per denier and the yarns had linear densities of 400 to 600 denier.

Comparative examples utilized the same polymer and the same spinning apparatus under substantially the same conditions, except that the drying tensions and the spinneret capillary sizes were different as shown in TABLE I.

The yarns made herein were woven into fabrics and the fabrics were assembled, using multiple layers as indicated in TABLE II, into ballistic test panels. The fabrics were all plain weave and had a variety of weave counts as, also, indicated in TABLE II. The number of fabric plies in each sample was selected to yield an

areal density as near as possible to 3.42 Kgrams per square meter (0.7 pounds per square foot) and the plies were sewn together to form unitary structures for the ballistics V_{50} testing. Results are shown in TABLE II and, graphically, in the Figure.

TABLE I

	Invention		Comparative Examples						
Conditions	1	2	A	B	C	D	E	F	G
Capillary Diam (mil)	2.0	2.0	2.5	2.0	2.5	2.5	2.5	2.5	2.0
No. filaments	266	400	133	133	266	500	560	666	532
Drying tension (gpd)	3.5	3.5	0.7	0.3	2.0	2.1	2.1	2.1	3.5
Yarn Properties									
Yarn Denier	400	600	200	200	400	750	840	1000	840
Tenacity (gpd)	28.5	28.2	23	27	27	26.5	27	26.2	8.2
Elong. (%)	3.2	3.2	3.0	3.5	3.3	3.3	3.4	3.4	3.3
Modulus (gpd)	830	800	750	700	760	740	760	740	829

Fabrics made from the yarns were assembled in layers and tested for ballistic performance as described in Table II.

As seen in the Figure, V_{50} for yarn deniers of less than 300 and more than 750 are lower than for yarn deniers within that range and V_{50} for yarn tenacities less than 28 gpd are lower than for yarn tenacities above that value. The yarn denier and yarn tenacity limits for the ballistic protective fabric of this invention are graphically reproduced in the Figure.

TABLE II

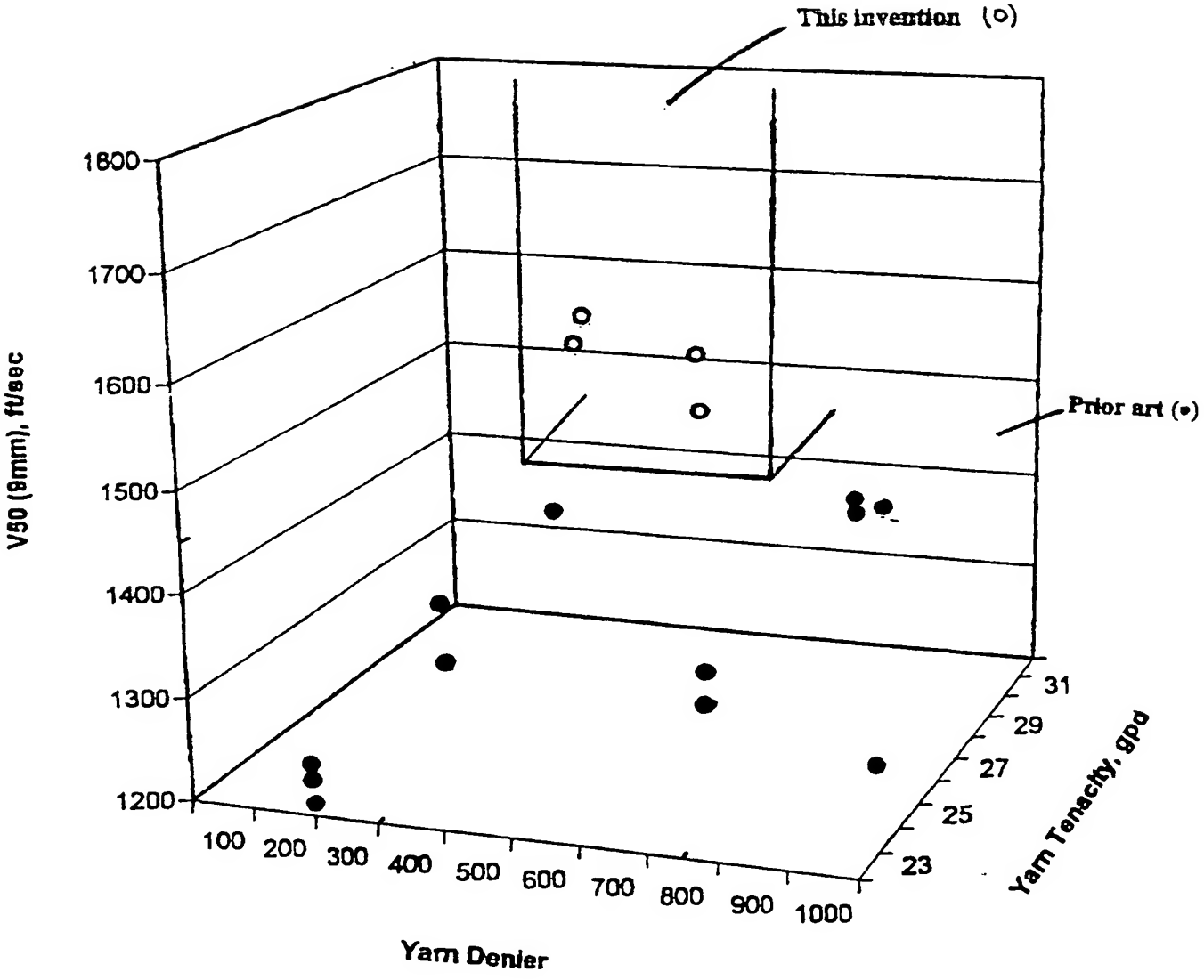
Example	Yarn Denier	Yarn Tenacity	Weave Count	No. of Plies	Areal Density	V_{50} (ft/sec)
1-1	400	28.5	31x31	32	0.73	1578
1-2	400	28.5	31x31	32	0.73	1553
2-1	600	28.2	31x31	21	0.71	1551
2-2	600	28.2	31x31	21	0.71	1485
A-1	200	23	40x40	49	0.72	1215
A-2	200	23	50x50	39	0.71	1244
A-3	200	23	63x63	30	0.70	1257
B-1	200	27	50x50	39	0.72	1312
B-2	200	27	70x70	27	0.71	1243
C	400	27	36x36	28	0.73	1424
D-1	750	26.5	31x31	17	0.72	1310
D-2	750	26.5	36x37	14	0.71	1281
E-1	840	27	31x31	16	0.72	1423
E-2	840	27	26x26	19	0.76	1438
F	1000	23	31x31	13	0.75	1285
G	840	28.2	26x26	18	0.72	1442

WHAT IS CLAIMED IS:

1. A ballistic protective fabric comprising yarn of at least 28 grams per denier (gpd) tenacity and a linear density of from 300 to 750 denier.

2. The fabric of Claim 1 wherein, when tested in accordance with MIL-STD-662e using 9mm full metal jacket hand-gun bullets weighing 124 grains, in layers to yield an areal density of 3.4 kilograms per square meter (0.7 pounds per square foot), exhibits a V_{50} of greater than 442 meters per second (1450 feet per second).

3. The fabric of Claim 1 wherein the yarn has a linear density of 400 to 600 denier.



FIGURE

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/19150

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F41H5/04

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 F41H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 09336 A (ALLIED SIGNAL INC) 28 April 1994 see page 6, line 24-28 see page 11, line 22-30 see page 20, line 6-18 see page 22, Table I ---	1-3
X	WO 87 03674 A (ALLIED CORP) 18 June 1987 see page 20, line 6-35 ---	1-3
X	WO 96 32621 A (DU PONT) 17 October 1996 see page 10, line 10-42 ---	1-3
X	EP 0 089 537 A (ALLIED CORP) 28 September 1983 see page 4, line 26-30 see page 6, line 12-27 see page 22, Table 10 --- -/--	1-3

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
25 February 1998	19/03/1998

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5 619 748 A (NELSON JEFF S ET AL) 15 April 1997 see column 4, line 30-49	1-3
X	WO 91 12136 A (ALLIED SIGNAL INC) 22 August 1991 see page 27, line 7-21	1-3
A	WO 93 20400 A (DOW CHEMICAL CO) 14 October 1993 see page 6, line 6-13 see page 7, line 32-35	1,3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

[redacted]rmation on patent family members

Int[redacted]nal Application No
PCT/US 97/19150

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9409336 A	28-04-94	DE 69310379 D	05-06-97
		DE 69310379 T	21-08-97
		EP 0664875 A	02-08-95
		JP 8502555 T	19-03-96
		US 5579628 A	03-12-96
WO 8703674 A	18-06-87	US 4681792 A	21-07-87
		CA 1263267 A	28-11-89
		DE 3689884 D	07-07-94
		DE 3689884 T	22-09-94
		EP 0287561 A	26-10-88
		JP 7049919 B	31-05-95
		JP 63502769 T	13-10-88
WO 9632621 A	17-10-96	US 5578358 A	26-11-96
		EP 0820577 A	28-01-98
EP 0089537 A	28-09-83	US 4403012 A	06-09-83
		US 4457985 A	03-07-84
		CA 1198563 A	31-12-85
		JP 2601444 B	16-04-97
		JP 58180635 A	22-10-83
US 5619748 A	15-04-97	NONE	
WO 9112136 A	22-08-91	CA 2075211 A	17-08-91
		JP 5503475 T	10-06-93
		NL 9120011 T	01-12-92
WO 9320400 A	14-10-93	AU 4767993 A	08-11-93
		CA 2131701 A	14-10-93
		EP 0769129 A	23-04-97
		JP 7505466 T	15-06-95